

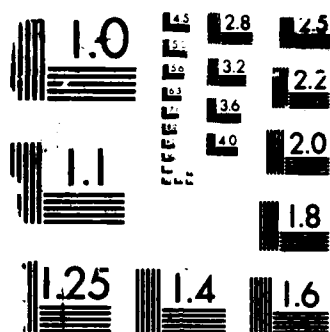
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Study of the Vibrational Modes of Subsurface Oxygen on Al (III)

Using Diode Laser Infrared Reflection-Absorption Spectroscopy

by

V.M. Bermudez, R.L. Rubinovitz and J.E. Butler

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STUDY OF THE VIBRATIONAL MODES OF SUBSURFACE OXYGEN ON Al (111) USING DIODE  
LASER INFRARED REFLECTION-ABSORPTION SPECTROSCOPY

V.M. Bermudez, R.L. Rubinovitz\* and J.E. Butler

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ABSTRACT

Infrared reflection absorption spectroscopy (IRRAS), using polarization modulation and tunable diode laser excitation, has been applied to the study of the vibrational modes of subsurface oxygen on Al (111). The dependence of the spectra on O<sub>2</sub> exposure and on annealing has been investigated at a resolution of about 10-20 cm<sup>-1</sup> (1.2-2.5 meV) and correlated with Auger data. The absorption band (~780-920 cm<sup>-1</sup>) consists of overlapping bands at about 835 and 862 cm<sup>-1</sup> associated, respectively, with isolated sites and with clusters of such sites resembling Al<sub>2</sub>O<sub>3</sub>. The apparent shift of this band to higher energy with increasing coverage, observed at lower resolution (but higher sensitivity) in electron energy loss spectroscopy, is found to result from the change in relative intensity of the two modes.

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## INTRODUCTION

The subject of coverage-dependent vibrational shifts is currently of great interest<sup>1,2</sup>. Most of the experimental work has focused on CO adsorbed on single crystal metal surfaces. The shift of the C≡O stretch to higher energy with increasing coverage, which is observed in most cases, can often be understood in terms of resonant coupling. This consists<sup>1</sup> of either through-space "dipole" or through-substrate "vibrational" coupling which are physically different but mathematically equivalent. Coverage-dependent shifts can also be induced by non-resonant structural or chemical effects<sup>1</sup> which can be either positive or negative, and systems for which resonant and non-resonant interactions are both large exhibit complicated behavior<sup>3</sup>.

The case of O on Al (111) [and also on Al (100)], which has been studied extensively<sup>4-11</sup> using high-resolution electron energy-loss spectroscopy (EELS), is especially intriguing. O<sub>2</sub> dissociates on this surface to populate two types of adsorption sites<sup>12</sup>. One has an O atom above one of the two non-equivalent three-fold hollow sites (i.e., a "surface O"), and the other has an O at a trigonally distorted tetrahedral site between the first and second planes of Al (a "subsurface O"). Three stretching modes normal to the surface (P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub>) are observed<sup>6</sup>. P<sub>3</sub> (820 to 875 cm<sup>-1</sup>, depending on coverage) involves the subsurface O, P<sub>2</sub> (545 to 690 cm<sup>-1</sup>) the surface O and P<sub>1</sub> (~410 to 425 cm<sup>-1</sup>) the out-of-phase motion of both. This system affords an opportunity<sup>7</sup> to study coverage-dependent shifts in both surface and subsurface dipoles, for which both coupling and chemical effects might be very different. The ranges of values quoted above show that the shifts for P<sub>2</sub> and P<sub>3</sub> are very different (145 vs. 55 cm<sup>-1</sup>) and that the fractional shift in P<sub>2</sub> (almost 30% of the low-coverage value) is much larger than those typically observed<sup>1,2</sup> for CO (≤10%). The results for O/Al (111) are also in stark contrast with those<sup>13</sup> for O/Ni (100) which show a negative shift of 25% in the Ni-O frequency as coverage

obtained. The noise level in the "raw" spectra corresponded to  $\delta R/R \sim 0.03\%$ , vs.  $\sim 0.05\%$  in earlier work<sup>14</sup>, and smoothing further reduced this value to about 0.01%. The angle of incidence was  $\phi \sim 86^\circ$ .

All experiments were performed in a two-level stainless steel UHV chamber (base pressure  $< 2 \times 10^{-10}$  torr). The lower level included a single-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), LEED (low energy electron diffraction) optics, an ion gun and a quadrupole mass spectrometer. The upper level contained KBr infrared windows and a bakeable gas admission manifold. Cooling of the specimen (to  $\sim 110^\circ\text{K}$ ) in the IRRAS position was achieved, following published<sup>16,17</sup> designs, through contact between the sample stage and a liquid N<sub>2</sub> reservoir attached to the base flange of the manipulator.

The sample was a  $1 \times 0.2$  cm disk of 99.999% pure Al, oriented to within  $\pm 0.5^\circ$  of (111), which was rough polished (400-mesh grit), etched in nitric acid and cleaned ultrasonically in isopropanol. Radiation from a W coil  $\sim 0.4$  cm behind the sample was easily sufficient to anneal the Al. Temperature was measured with a chromel-alumel thermocouple buried in a small hole in the crystal. After outgassing for  $\sim 50$  hrs. at  $450-480^\circ\text{C}$ , the sample was subjected to repeated cycles of 1 hr. of Ar<sup>+</sup> ion bombardment (1 keV, 17  $\mu\text{A}$ ,  $\sim 60^\circ$  angle of incidence) and 1 hr. of annealing in UHV at  $450^\circ\text{C}$  until the total impurity level (C and O) was less than 0.005 monolayers. Following a series of O<sub>2</sub> exposures the sample was cleaned by a single sputter-anneal cycle. Studies of AES exposure dependence were performed with modulation amplitudes of 1 eV (Al LVV), 2 eV (O KLL) or 4 eV (Al KLL) and a primary beam of 3 keV and 2-10  $\mu\text{A}$ . Sharp LEED patterns of high contrast were obtained, at  $E_p \sim 30$  eV, for the clean surfaces. The same series of experiments was also performed on a  $2.5 \times 0.2$  cm disk, of similar orientation and purity, mechanically polished to  $1\mu$ . Repeated sputtering and annealing of this surface yielded a dull hazy appearance<sup>4</sup>. Similar results were obtained, except that the oxygen uptake was

somewhat more rapid, with saturation occurring at ~20 vs. ~50 L, and the IRRAS linewidth at saturation was narrower.

O<sub>2</sub> exposures (in Langmuirs, L, where 1 L = 10<sup>-6</sup> torr-sec = 3.59 x 10<sup>14</sup> O<sub>2</sub>/cm<sup>2</sup> at 300°K) were performed using dynamic backfills of 99.995% O<sub>2</sub>. Residual gas analysis showed impurity levels of ~1% each for H<sub>2</sub>O, CO and CO<sub>2</sub>. CO (and, presumably, CO<sub>2</sub>) is found<sup>10</sup> not to react with Al in the absence of electron beam irradiation. H<sub>2</sub>O is reported<sup>18</sup> to react with clean Al surfaces only about 4 times faster than does O<sub>2</sub>; hence, in the O<sub>2</sub> exposure range of interest in this work (20-100 L), the effect of the H<sub>2</sub>O impurity is negligible. For IRRAS, exposures were carried out at pressures of 1-5x10<sup>-7</sup> torr, and a microcomputer monitoring the nude ionization gauge gave continuous readings of integrated pressure vs. time, assuring reproducible exposures. The start of the IRRAS scans was delayed for ~10 min., following each O<sub>2</sub> exposure, since previous work<sup>14</sup> indicates that O is mobile on the Al surface at room temperature, and several minutes are required for the work function to stabilize after evacuation of the O<sub>2</sub>. AES after O<sub>2</sub> exposure showed small levels of C contamination [(C KLL)/(O KLL) peak-to-peak ratio of ~0.03 after 50 L].

## RESULTS and DISCUSSION

### (a) Auger Measurements

AES data vs. O<sub>2</sub> exposure, obtained in a separate series of experiments, are shown in Fig. 1. The sample temperature was in the 50-90°C range since measurements were started soon after annealing. AES was done to "calibrate" our sample and experimental conditions to obtain a basis for relating our IRRAS data with previous EELS studies. Although the total O coverage can be estimated, it is not possible, using AES, to determine the relative amount of surface and subsurface O.

Beginning in the 0 L limit, one notes that the clean-surface Al L<sub>2,3</sub>VV



(O KLL) AES intensity lies above (below) the extrapolation of the lines through the points from 1 to 15 L. This effect has been noted previously<sup>19</sup> and suggests a very rapid adsorption process, saturating at  $\sim 1$  L, which may involve defect sites or steps. From 1 to 15 L, the metallic Al  $L_{2,3}VV$  and the Al KLL intensities decrease linearly and the O KLL increases linearly. Near the 15 L break-point (change in slope) the  $Al^{+3}$   $L_{2,3}VV$  peak is first detectable. The exposure dependence of this feature extrapolates to an onset at  $\sim 10$  L. The  $Al^{+3}$  and O KLL structures increase in intensity up to a second break-point at  $\sim 35-45$  L; concurrently, the metallic Al  $L_{2,3}VV$  and the Al KLL decrease (with smaller slopes than below 15 L). From  $\sim 45$  to 240 L, changes in the AES intensities are relatively slow, and the existence of further break-points above 50 L is uncertain. The data agree qualitatively with earlier results<sup>19,20</sup>; although, the exposures at which break-points occur differ among various studies which may reflect differences in ionization gauge calibration, surface condition, electron beam effects, etc. These results are consistent with the interpretation of Chen et al.<sup>5</sup> for data obtained at 135°K. From 0 to 15 L (in Fig. 1) is the "chemisorption" phase in which isolated surface and subsurface sites are populated. Surface "oxidation" begins at  $\sim 15$  L as shown by the appearance of the 52 eV  $Al^{+3}$   $L_{2,3}VV$ , indicative of multiply coordinated Al ions as in  $Al_2O_3$ , with continued rapid growth of the O KLL. By  $\sim 45$  L oxidation of the surface is complete, in the sense that all energetically favorable sites have been occupied, and further uptake (at room temperature) is either slow or occurs subsurface at a depth inaccessible to AES.

#### (b) IRRAS Lineshape

A quantitative description of the IRRAS lineshape, which will be useful in the following discussion, is briefly summarized here. In the thin-film limit the oxidation-induced change in  $\delta R/R$ , as defined above, is given by<sup>2</sup>

$$\Delta\left(\frac{\delta R}{R}\right) = \left(\frac{\delta R}{R}\right)_{\text{ox}} - \left(\frac{\delta R}{R}\right)_{\text{clean}} = \left(1 + R_s/R_p\right)^{-1} \frac{8\pi d \sin\phi \tan\phi}{\lambda} \text{Im}\left[\frac{-1}{\tilde{\epsilon}(\omega)}\right] \quad (1)$$

where  $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$  is the complex dielectric function of the "overlayer" of thickness  $d$ , and  $\lambda = 1/\omega$  is the infrared wavelength. For Al in the mid-IR at  $\phi = 86^\circ$ ,  $R_s/R_p$  is a constant equal to  $\sim 1.2$ . The overlayer is defined by whatever changes on the surface as a result of O<sub>2</sub> adsorption. Hence it includes the adsorbed layer as well as, implicitly, the effects of any modification of the substrate (e.g., impurity-induced relaxation or reconstruction, decrease in free electron density, etc.). In the region of strong adsorbate absorption the Lorentzian dielectric function is given by

$$\tilde{\epsilon}_L(\omega) = \epsilon_0 + \sum_j \tilde{\epsilon}_L^j(\omega) = \epsilon_0 + \sum_j \frac{4\pi\omega_j^2 S_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega} \quad (2)$$

where  $\epsilon_0$  is the non-resonant component of the dielectric function, and  $S_j$ ,  $\omega_j$ , and  $\gamma_j$  are the dipole strength, resonant frequency and natural linewidth, respectively, of the  $j$ -th mode. The absorption band may also be inhomogeneously broadened by factors, such as residual disorder, causing a slight non-equivalence between nominally identical binding sites. Further broadening is, of course, produced by the finite IRRAS resolution. These effects can be represented by a convolution of each Lorentzian with a normalized gaussian, giving a dielectric function of the form

$$\tilde{\epsilon}(\omega) = \epsilon_0 + \sum_j \left\{ \frac{1}{\sqrt{2\pi}\sigma_j} \int_0^\infty \tilde{\epsilon}_L^j(\omega') e^{-(\omega-\omega')^2/2\sigma_j^2} d\omega' \right\} \quad (3)$$

A least-squares fitting routine was used to fit Eqs. (1)-(3) to the IRRAS data. A linear term ( $a + b\omega$ ) was added to the right-hand side of Eq. (1), to account for changes in the background caused by long-term drift in the optical system and the parameters determined as part of the fit.

### (c) IRRAS Exposure Dependence

Figs. 2-4 summarize the IRRAS results, the essential features of which were reproduced in several (four or five) repetitions of the experiment. At the lowest exposures (15-20 L) for which useable data could be obtained, two overlapping, barely resolved bands are observed at roughly 840 and 865  $\text{cm}^{-1}$ . The intensity of the 865  $\text{cm}^{-1}$  mode increases, relative to that at 840  $\text{cm}^{-1}$ , with increasing  $\text{O}_2$  exposure and becomes dominant above ~40 L. This is apparent as a gradual gain in intensity on the high energy side of the original band. Little change occurs between 50 and 100 L, consistent with AES. Neither band shows a significant shift in frequency with coverage. This is emphasized by the use of the lineshape fitting described above to estimate, with more precision than can be attained by visual inspection, the energies and relative intensities.

The values thus obtained for the resonant frequencies are  $862 \pm 7$  and  $835 \pm 5$   $\text{cm}^{-1}$ , the uncertainties reflecting those in the energy calibration and fitting. The gaussian full-width at half-maximum ( $\text{FWHM} = 2.35\sigma$ ) for the 862  $\text{cm}^{-1}$  mode is consistently (i.e., independent of starting choice of fitting parameters) about twice that of the 835  $\text{cm}^{-1}$  band. Correcting for the contribution from instrumental resolution gives linewidths of about 75 and 35  $\text{cm}^{-1}$ , respectively. This indicates significant inhomogeneous broadening, consistent with suggestions<sup>4</sup> of a distribution of surface and subsurface O sites at exposures (>15 L in the present case) for which the 52 eV  $\text{Al}^{+3}$  AES peak is observable. The width of the 862  $\text{cm}^{-1}$  band is also comparable to that found for the LO mode in very thin annealed  $\text{Al}_2\text{O}_3$  films<sup>21,22</sup>. The integrated intensity of the IRRAS band increases by a factor of ~1.5 from 21 to 104 L  $\text{O}_2$ , in good agreement with the corresponding increase (factor of 1.7) in the O KLL AES intensity. This is in contrast to systems<sup>1,3</sup> such as  $\text{CO}/\text{Cu}(111)$  which show a sub-linear variation of IRRAS intensity with adsorbate coverage resulting from the mutual screening of the dipoles from the external field.

Following a 20 L O<sub>2</sub> exposure, a series of "flash" anneals was carried out, in 50°C steps from 100 to 300°C, by raising the sample to the desired temperature over about 2 min. then shutting off the heater, after which the sample cooled to the base temperature (~35°C) in about 10 min. The results, summarized in Fig. 4, show the gradual increase in the relative intensity of the 862 cm<sup>-1</sup> component with increasing annealing temperature. This effect is apparent at temperatures well below the reported threshold<sup>4</sup> (500°K = 227°C) for thermally driven conversion of an adsorbed oxygen layer to Al<sub>2</sub>O<sub>3</sub>. The change in the spectrum with annealing, similar to that observed with increasing O<sub>2</sub> exposure, indicates depopulation of one type of O adsorption site in favor of the other. AES for a similar series of anneals indicates an increase (decrease) in the 52 eV Al<sup>3+</sup> (68 eV metallic Al) L<sub>2,3</sub>VV signal with no change (<10%) in O KLL, showing that the IRRAS changes do not result from increased O coverage. The sloping background after annealing is believed to result from very small changes in sample position during thermal cycling.

EELS data<sup>4,5</sup> at lower resolution (80-100 cm<sup>-1</sup>) but higher sensitivity, for a similar range of O coverage, show a single mode shifting from 820 to 865 cm<sup>-1</sup>. At an O coverage for which the Al<sup>3+</sup> AES peak is barely detectable the EELS peak<sup>4</sup> is at 830 cm<sup>-1</sup>. The results in Figs. 2 and 3 indicate that above this coverage the apparent shift derives from the changing relative intensity of two overlapping bands. It remains a possibility that the EELS shift (820 to 830 cm<sup>-1</sup>) below this coverage is related to dipole coupling or chemical/structural effects. If this is the case, one can estimate an upper limit of ~10 cm<sup>-1</sup> on the magnitude of such a coverage-dependent shift.

Since the 835 cm<sup>-1</sup> mode is close to the P<sub>3</sub> energy at very low coverage and has a smaller FWHM than does the 862 cm<sup>-1</sup> band, we associate it with isolated Al-O-Al subsurface sites. Likewise, the 862 cm<sup>-1</sup> mode is associated with multiply O-coordinated sites resembling patches of "rudimentary" Al<sub>2</sub>O<sub>3</sub>. Such sites cannot be identical to bulk Al<sub>2</sub>O<sub>3</sub> since the mode frequency is much

lower than that observed<sup>21</sup> ( $910\text{ cm}^{-1}$ ) for  $\text{Al}_2\text{O}_3$  films only  $5\text{ \AA}$  thick sputter-deposited onto Au.

Finally, IRRAS data were obtained at  $110^\circ\text{K}$  in order to determine the validity of comparing low-temperature EELS data<sup>4-6</sup> for  $\text{P}_3$  with those obtained at room temperature. First, a background spectrum of the clean surface was recorded at  $110^\circ\text{K}$ . After warming to  $300^\circ\text{K}$  and a  $50\text{ L O}_2$  exposure (followed by a 10 min. wait) the sample was again cooled to  $110^\circ\text{K}$  and another spectrum recorded. The difference spectrum shows a single broad band at  $\sim 860\text{ cm}^{-1}$ , similar to data taken at  $300^\circ\text{K}$ . The absence of significant temperature dependence in the linewidth is further suggestive of inhomogeneous broadening.

Several unsuccessful attempts were made to detect the surface Al-O mode ( $\text{P}_2$ ). Specular EELS data<sup>6</sup> for a "saturated" surface at  $300^\circ\text{K}$  indicate approximately equal intensity for  $\text{P}_2$  and  $\text{P}_3$ . Failure to detect  $\text{P}_2$  in an optical experiment could be explained by an additional contribution from impact scattering in EELS. However, there is no clear evidence for such an effect in the off-specular EELS<sup>7</sup> of very thin  $\text{Al}_2\text{O}_3$  films.

In conclusion, we find no compelling evidence for dipole coupling effects in the coverage dependence of either the energy or intensity of the  $\text{P}_3$  subsurface vibrational mode of O/Al (111). Most, if not all, of the  $\sim 55\text{ cm}^{-1}$  shift to higher energy with increasing coverage, observed at lower resolution (but higher sensitivity) in EELS, is found to result from the changing relative intensity of modes at about  $835$  and  $862\text{ cm}^{-1}$  assigned, respectively, to isolated Al-O-Al sites and to clusters of such sites. An upper limit of  $\sim 10\text{ cm}^{-1}$  is estimated for the coverage-induced shift in the isolated Al-O-Al mode.

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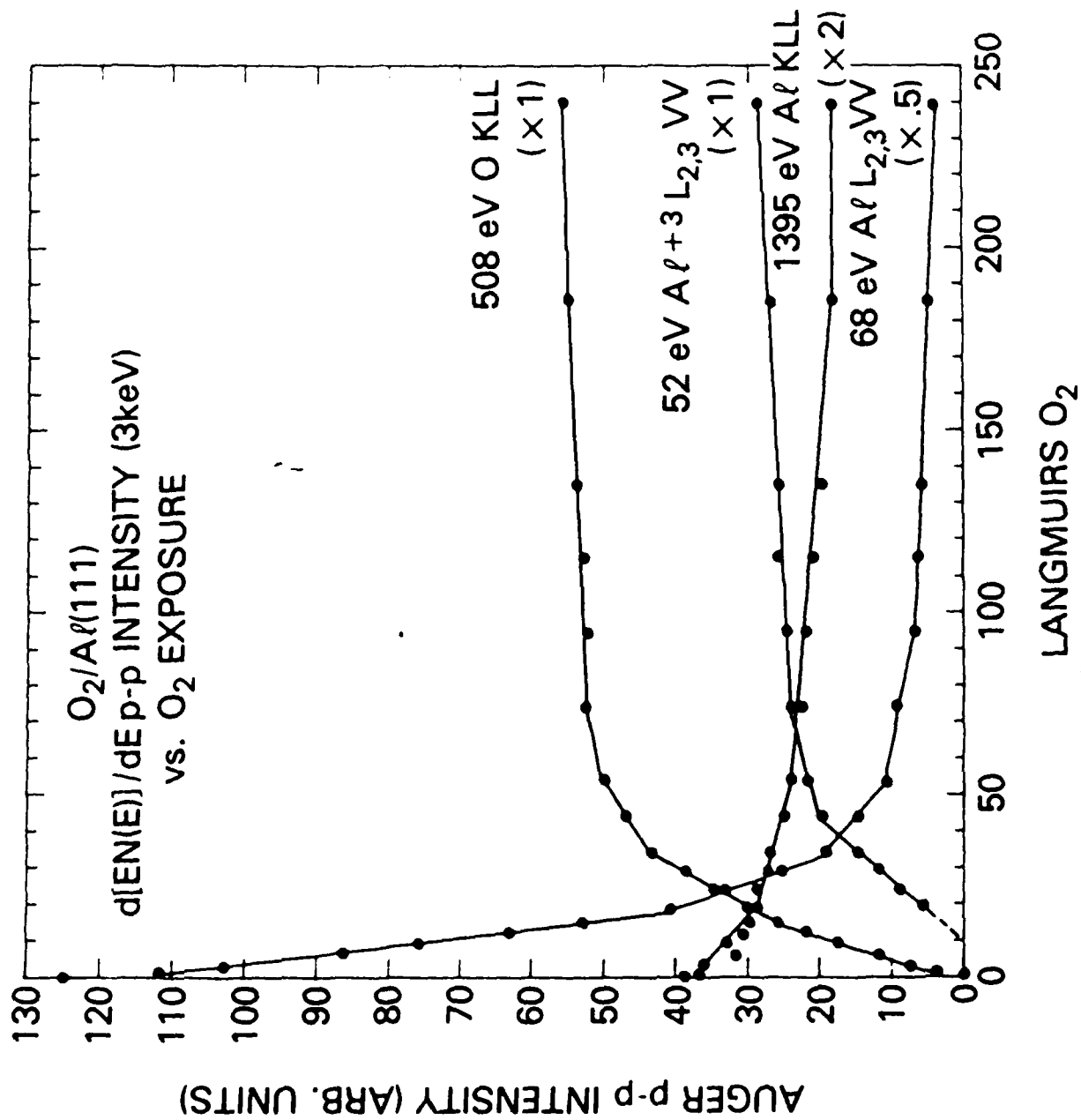
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#### FIGURE CAPTIONS

1. Variation in the Auger peak-to-peak amplitudes with O<sub>2</sub> exposure for Al (111) at ~50-90°C. The numbers in parentheses are the relative scale factors adjusted for the differences in modulation amplitude. Only the break-points (slope changes) below 50 L are considered reliable. Pressures were in the  $1-5 \times 10^{-8}$  torr range during the initial small (1-5 L) exposure steps.
2. IRRAS data, vs. exposure at 35°C, for O/Al (111) in the region of the sub-surface (P<sub>3</sub>) Al-O stretching mode. The data represent the change in  $\delta R/R$  (see text) induced by O<sub>2</sub> exposure. The resolution is ~20 cm<sup>-1</sup> (2.5 meV). Absorption increases in the downward direction. The vertical dashed lines indicate the approximate peak energies of the two components. The zero level of each spectrum is indicated by a horizontal dashed line.
3. Lineshape fits to the data in Fig. 2. The horizontal dashed lines are the zero-levels for each spectrum after subtraction of a linear background (obtained as part of the fit). The points are the data and the solid line the least-squares fit. The individual oscillator bands are also shown.
4. Effect of annealing (see text) of Al (111) following a 20 L O<sub>2</sub> exposure at 35°C. (a) unannealed, (b) 150°C anneal and (c) 250°C anneal. The background changes after annealing are believed to result from small shifts in sample position during thermal cycling.

Fig 1





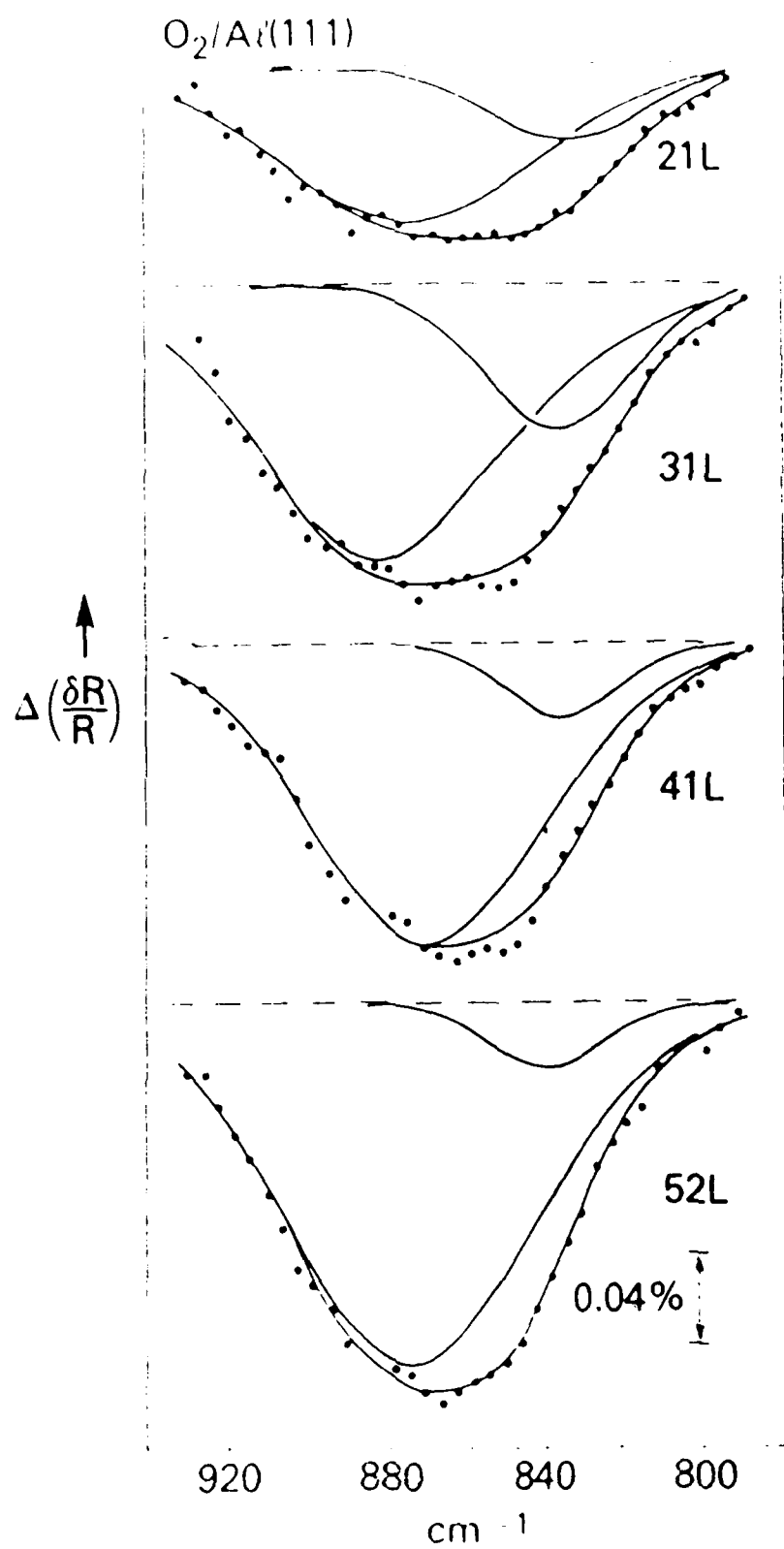


Fig 3

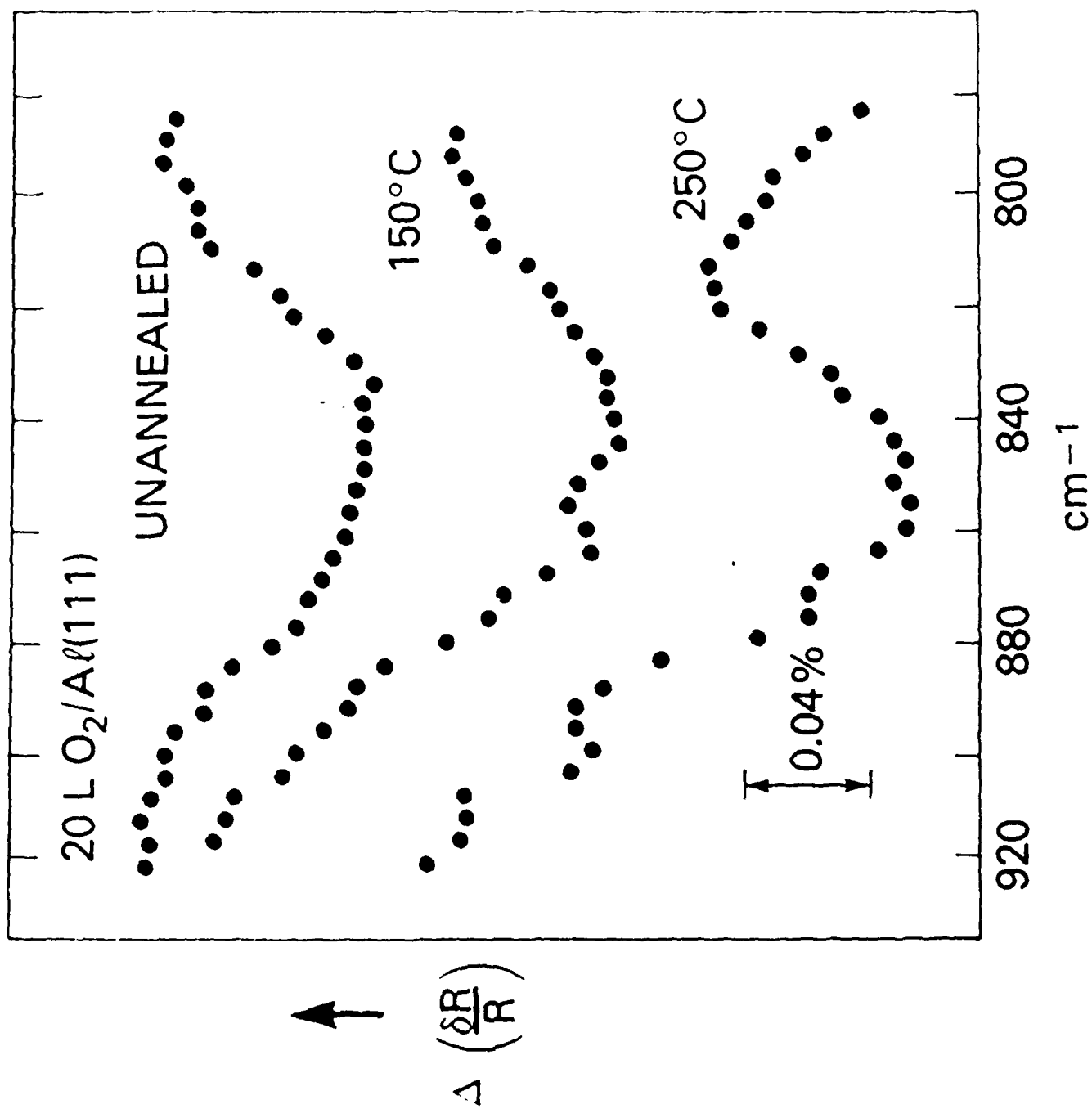


Fig 4

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